METHOD FOR REMOVING IMPURITY IN RESIN FOR ELECTRONIC PART

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Abstract of **JP6032814**
PURPOSE:To provide a process for the removal of impurities in a resin for electronic part and capable of easily decreasing the concentration of each metallic impurity element to <=0.1ppm. CONSTITUTION:An ultra-high purity positive-type resist composition having a metallic impurity element concentration of e.g. as low as several tens ppb can be produced by a process (I) to remove impurities from an impurity- containing resin for electronic part by a hot-water treatment and/or a dilute acid treatment of the resin to obtain a resin free from impurity and a process (II) to separate the purified resin while preventing the intrusion of impurities and to dry the separated resin.

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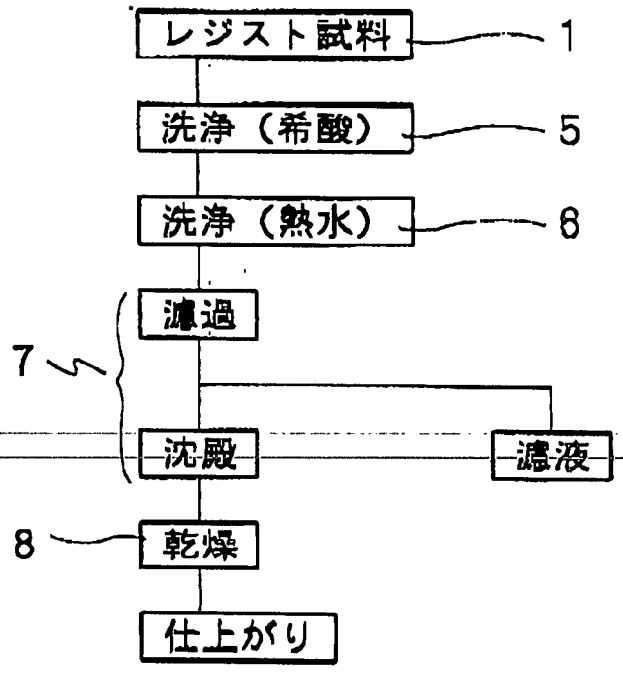
(54)【発明の名称】　電子部品用樹脂中の不純物除去方法

(57)【要約】

【目的】　電子部品用樹脂中の不純物を容易に、かつ金属系の各不純物元素濃度を 0.1 ppm以下に除去・低減化することが可能な、電子部品用樹脂中の不純物除去方法の提供を目的とする。

【構成】　不純物を含有する電子部品用樹脂を少なくとも熱水処理もしくは希酸処理のいずれか一つの処理を施し含有不純物を除去する工程と、前記含有不純物の除去された電子部品用樹脂を不純物侵入を防止しながら分離し、乾燥処理する工程とを具備することを特徴とし、たとえば金属系の不純物元素濃度が数10 ppbレベルの超高純度ポジ型レジスト組成物と成し得る。



【特許請求の範囲】
【請求項１】 不純物を含有する電子部品用樹脂を少なくとも熱水処理もしくは希酸処理のいずれか一つの処理を施し含有不純物を除去する工程と、
前記含有不純物の除去された電子部品用樹脂を不純物侵入を防止しながら分離し、乾燥処理する工程とを具備して成ることを特徴とする電子部品用樹脂中の不純物除去方法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は、電子部品用樹脂中の不純物除去方法に係り、特に樹脂中に含まれる鉄やナトリウムなどの金属系不純物の除去・低減に有効な電子部品用樹脂中の不純物除去方法に関する。
【０００２】
【従来の技術】たとえば集積回路の製造においては、能動素子などのパターニングに当たり、一般的に環化イソプレンゴムを素材としたネガ型レジスト、あるいはノボラック樹脂を素材としたポジ型レジストが使用されている。そして、近年では、集積回路の集積度上昇に伴い、解像度のすぐれたポジ型感光樹脂が多用される状況になってきている。
【０００３】しかし、前記フォトレジスト樹脂中にアルカリ金属や、重金属などの金属系の不純物が存在する（含有されている）と、たとえその量が極微量であったとしても、絶縁酸化膜の耐圧不良およびPN接合リーク不良などを引き起こす原因となる。つまり、ULSIの製造工程で用いたフォトレジスト樹脂に、含有されていた極微量の金属系不純物が、最終的に製造されたUSLIの機能的な信頼性に重要な影響を与える。したがって、この種のフォトレジスト樹脂においては、可能な限り金属系不純物を除去することが望まれている。
【０００４】上記の要求に対して、一般的には図２に示す手順での純水（常温）による洗浄操作で、フォトレジスト樹脂中の不純物の除去・低減化を図っている。具体的には、たとえばアルコールやアセトンなどの有機溶媒にフォトレジスト樹脂を溶解し、この樹脂溶液１を多量の撹拌純水（常温）中に滴下して撹拌洗浄処理２した後、樹脂成分のみを沈殿・濾別分離処理３して乾燥処理４する方法、あるいは酢酸エチルやトルエンなどの非水溶性の溶媒にフォトレジスト樹脂を溶解し、その樹脂溶液を純水（常温）と激しく撹拌洗浄処理して不純物のみを抽出除去してから、前記非水溶性の溶媒を除去し、乾燥処理４する方法などが挙げられる。そして、これらの洗浄操作方法は、通常、前記の洗浄操作を反復し、許容範囲まで不純物濃度を低下させている。
【０００５】なお、上記ではフォトレジスト樹脂における金属系不純物の影響、および不純物の除去・低減化手段について例示したが、たとえば半導体装置の封止用樹脂、保護膜用樹脂、もしくは多層配線の層間絶縁用樹脂などの場合も、適用（使用）する装置などに要求される性能・機能の点から無視し得ない問題である。
【０００６】
【発明が解決しようとする課題】上記常温の純水を用い洗浄する方法は、樹脂中に含有されている不純物の除去・低減化を図り得るが、未だアルカリ金属元素や重金属元素の除去効率が悪く、たとえば金属系の各不純物元素濃度を 0.1 ppm以下に除去・低減化することは困難であった。つまり、常温の純水による洗浄操作の繰り返しで、金属系の不純物元素濃度をある程度までは比較的容易に低減しえるが、たとえば 1 ppm程度の極微量に達した時点以降においては、前記洗浄操作の繰り返し回数は大幅に増やしても、その割に金属系の不純物元素濃度の除去・低減率が低く、実用的な面で限界を認めざるを得ないからである。
【０００７】本発明はこのような事情に対処してなされたもので、電子部品用樹脂中の不純物を容易に、かつ金属系の各不純物元素濃度を 0.1 ppm以下に除去・低減化することが可能な、電子部品用樹脂中の不純物除去方法の提供を目的とする。
【０００８】
【課題を解決するための手段】本発明に係る電子部品用樹脂中の不純物除去方法は、不純物を含有する電子部品用樹脂を少なくとも熱水処理もしくは希酸処理のいずれか一つの処理を施し含有不純物を除去する工程と、前記含有不純物の除去された電子部品用樹脂を不純物侵入を防止しながら分離し、乾燥処理する工程とを具備して成ることを特徴とする。
【０００９】そして、この発明はフォトレジスト樹脂など電子部品用樹脂において、微量含有している金属不純物の除去・低減の方策を鋭意、検討・研究した結果、熱水処理もしくは希酸処理いずれかの処理を施した場合、樹脂中の金属不純物元素濃度をそれぞれ 0.1 ppm以下に、容易かつ確実に除去・低減化し得るとの知見に基づいてなされたものである。
【００１０】本発明において、被処理体となる不純物を含有する電子部品用樹脂としては、従来公知のいずれの方法で製造されたレジスト樹脂であってもよく、たとえばポリイソプレンやポリブタジェンなどのゴム系レジスト樹脂、アクリル酸エステルやメタクリル酸エステルなどのアクリル系レジスト樹脂、ノボラックなどのフェノール系レジスト樹脂などが挙げられる。そして、含有されている不純物濃度が感度、もしくはパターンプロファイルに敏感に影響を与えるレジスト樹脂、たとえば環境に対して敏感な性質を有する化学増幅型レジスト樹脂を被処理体とした場合、さらに有効である。
【００１１】このような化学増幅型レジスト樹脂としては、たとえばフェノールノボラック樹脂型、クレゾールノボラック樹脂型、キシレノールノボラック樹脂型、ビニルフェノール樹脂、イソプロペニルフェノール樹脂、

ビニルフェノールとアクリル酸，メタクリル酸誘導体，アクリロニトリル，スチレン誘導体などとの共重合体、イソプロペニルフェノールとアクリル酸，メタクリル酸誘導体，アクリロニトリル，スチレン誘導体などとの共重合体などがあり、具体的には、たとえばポリ（p-ヒニルフェノール）、p-イソプロペニルフェノールとニトリルとの共重合体（共重合比 1:1）、p-イソプロペニルフェノールとスチレンとの共重合体（共重合比 1:1）、p-ビニルフェノールとメチルメタクリレートとの共重合体（共重合比 1:1）、p-ビニルフェノールとメチルスチレンとの共重合体（共重合比 1:1）などが挙げられる。

【００１２】さらに、前記レジスト樹脂においては、現像液溶解性の制御、あるいは感光性の付与を目的として、反応試薬にアルカリ金属化合物などを用いて重合体の水酸基を、たとえばアセトキシ，ホルミロキシ，メタクリルアニリド，o-ニトロベンジル，ジヒドロピリジル，o-キノンジアジドスルホン酸，アクリロイル，ジアゾニウム，スルホニウム，ヨウドニウム，有機ハロゲン化物などの感光性置換基、あるいはカルボン酸の tert-ブチルエステル， tert-ブチルカルボナートなどの第三級炭素を有する保護基、シクルヘキシル，sec-ブチル基，イソプロピル基などの第二級炭素を有する保護基、トリアルキル基，フェニルシリル基，テトラヒドロピラニル基，メチルメトキシ基などの保護基で置換した場合などの処理に適する。

【００１３】上記電子部品用樹脂中に含有されている不純物としては、たとえば鉄（Fe）、ナトリウム（Na）、カリウム（K）、銅（Cu）などが挙げられ、これら金属の不純物中、たとえば鉄（2+ もしくは 3+）、ナトリウム（1+）、カリウム（1+）、銅（1+ もしくは 2+）のようにイオン表示されるものである。

【００１４】本発明において使用する熱水（純水）、酸および溶媒などは、可能な限り高純度であることが必要で、それぞれ金属不純物濃度として、たとえば鉄：5ppb 以下、ナトリウム：10ppb 以下、カリウム：10ppb 以下、銅：5ppb以下が望ましい。そして、所要の洗浄処理に熱水（純水）を用いる場合の温度条件は、高温にするほど洗浄効果が向上することから、その温度を35℃程度以上、好ましくは40℃以上でにすることにより熱水による有効性が現れる。上限温度については被処理樹脂が熱分解を起さない範囲に設定することが必要で、一般的に被処理樹脂の熱分解温度より20℃以下を上限とすることが好ましい。また、熱水（純水）の使用量は特に制限ないが、より十分な洗浄効果を達成するためには、被処理樹脂量と同量以上に選択することが望ましい。

【００１５】一方、所要の洗浄処理に希酸水溶液を用いる場合、その酸濃度は被処理樹脂の酸に対する安定性など考慮して選択・設定する。たとえば酸架橋性あるいは酸分解性基を有する化学増幅型レジスト材料のときは、0.1～0.5M程度に設定される。そして、この種の希酸水溶液は、高純度の純水に、同じく高純度のたとえば硝酸，塩酸，フッ酸，クエン酸，酒石酸，乳酸などから選択された少なくとも１種の酸を所要量添加して、溶液化することにより調製し得る。なお、この希酸水溶液による洗浄処理は、常温で行ってもよいが、希酸水溶液による洗浄処理系を、たとえば40℃以上に加熱保温することにより、金属不純物をさらに効率的に除去・低減し得る。

【００１６】また、いずれの場合も、洗浄処理系のpH調整もしくは有機溶媒の選択（被処理樹脂を溶液化しての洗浄処理）などによって、たとえばクロム，亜鉛，銅の除去・低減を成し得る。

【００１７】本発明においては、前記洗浄処理など一連の操作で使用する洗浄装置（容器や器具）、分離装置、乾燥装置などが新たな汚染源となることを回避するため、不純物が溶出しない材質製、たとえばテフロン製や合成石英製（もしくはこれらでコーテングした構成）などを用いたり、作業環境（雰囲気）を考慮することは勿論である。

【００１８】

【作用】上記本発明方法によれば、たとえばナトリウムやカリウムなどの不純物を含有する電子部品用樹脂を、先ず熱水（純水）もしくは希酸水溶液と接触させ、洗浄処理を行う。そして、熱水（純水）による洗浄処理の場合、その熱により活性化エネルギーが向上し、含有されているナトリウムやカリウムなど溶出し易い元素は、速やかにイオン化して熱水中に容易に移動し、樹脂から分離されるので、電子部品用樹脂中の不純物の除去・低減が速成される。また、希酸水溶液で洗浄処理した場合も、希酸水溶液中の陰イオンが不純物であるたとえば鉄（2+ もしくは 3+）、銅（1+ もしくは 2+）などの陽イオンと速やかに反応して樹脂から分離されるので、電子部品用樹脂中の不純物の除去・低減が速成される。そして、この希酸水溶液で洗浄処理においても、加熱した場合は活性化エネルギーが向上し、不純物の除去・低減化の効率が高められる。なお、ここで被処理樹脂が粉末である場合よりも、溶液の場合の方が均一に洗浄されるため、不純物の除去効率は一般的に高くなる。

【００１９】

【実施例】以下実施例により本発明をさらに具体的に説明するが、本発明はこれらの実施例に限定されるものでなく、要旨を逸脱しない範囲で適宜変形して実施し得ることは勿論ある。

【００２０】実施例１

先ず、不純物濃度が、Na：20ppm，K：30ppm，Fe：10ppm，Cr：50ppm，Cu：10 ppmのm-クレゾールノボラック樹脂 100 gをテフロン製容器に収容し、さらに 0.5M酢酸水溶液 500 gを加え、60℃に加温（加熱）保持した状態で10分間激しく振とう攪拌し洗浄処理した。その後、テフロン製フィルターを用いて、前記樹脂分を濾取

し、上記洗浄処理を再度施してから、テフロン製フィルターで樹脂分を濾取した。なお、このとき２１の純水を用いて前記洗浄処理に使用した酢酸を十分に取り除いた。

【００２１】前記洗浄処理し、かつ濾取した樹脂分を真空乾燥器内に収容し、50℃で２日間乾燥処理して、樹脂中の不純物除去を終了した。このようにして不純物除去処理を行った樹脂粉末中の不純物濃度をフレームレス原子吸光装置により測定したところ、Na：10ppb，K：20ppb，Fe：50ppb，Cr：10ppb，Cu：10ppb と大幅に除去・低減していた。

【００２２】なお、m-クレゾールノボラック樹脂 100 gを酢酸エチル400gに溶解して調製した溶液の形で、上記洗浄処理条件に準じた表１に示す条件で、熱水による洗浄処理（実施例１ａ）、熱水ー常温酸溶液による洗浄処理（実施例１ｂ）、熱水ー熱酸溶液による洗浄処理（実施例１ｃ）、熱酸溶液による洗浄処理（実施例１ｄ）をそれぞれ行った結果を表２に実施例１の場合と併せて示す。

【００２３】上記実施例から分かるように、洗浄処理系を常温に設定した場合に比べ、加温（加熱）保持した場合の方が不純物除去効果が高く、また熱水洗浄の場合は、ナトリウム、カリウムの除去効果が大であった。さらに、図１にフローチャートで示すように、上記実施例において、洗浄処理工程５の後、熱水洗浄工程６を付加し、その後濾過・分離工程７、乾燥処理工程８を行った場合は、前記不純物の除去・低減がさらに効果的になされた。

【００２４】実施例２

先ず、不純物濃度が、Na：100ppm，K：300ppm，Fe：10ppm，Cr：4.0ppm，Cu：1.0ppmのtert-ブトキシカルボニル化ヒニルフェノール樹脂 100 gを酢酸エチル 400 gに溶解して調製した溶液をテフロン製容器に収容し、さらに0.5M酢酸水溶液 500 gを加え、40℃に加温（加熱）保持した状態で10分間激しく振とう撹拌し洗浄処理した。その後、30分間静置して樹脂溶液と酸水溶液の２層分離を行い、上層の樹脂溶液を分取した。この樹脂溶液から溶媒（酢酸エチル）を留去した後、アセトン 400 gで再度溶液化してから、３１の純水中に滴下して再沈殿させた後、テフロン製フィルターを用いて、前記樹脂分を濾取し、その濾取した樹脂分を真空乾燥器内に収容し、50℃で２日間乾燥処理して、樹脂中の不純物除去を終了した。このようにして不純物除去処理を行った樹脂粉末中の不純物濃度をフレームレス原子吸光装置により測定したところ、Na：60ppb，K：300ppb，Fe：100ppb，Cr：20ppb，Cu：10ppb と大幅に除去・低減していた。

【００２５】なお、tert-ブトキシカルボニル化ヒニルフェノール樹脂を溶液とせず粉末のの形で、上記洗浄処理条件に準じた表１に示す条件で、熱水による洗浄処理（実施例２ａ）、熱水ー常温酸溶液による洗浄処理（実施例２ｂ）、熱水ー熱酸溶液による洗浄処理（実施例２ｃ）、熱酸溶液による洗浄処理（実施例２ｄ）をそれぞれ行った結果を表２に実施例２の場合と併せて示す。

【００２６】上記実施例から分かるように、洗浄処理系を常温に設定した場合に比べ、加温（加熱）保持した場合の方が不純物除去効果が高く、また熱水洗浄の場合は、ナトリウム、カリウムの除去効果が大であった。

【００２７】

【表１】

	樹脂	試料の状態	熱水の温度（℃）	希酸水溶液中の酸	酸濃度（M）	酸の温度（℃）	処理条件 時間（分）	処理条件 回数
実施例１	樹脂Ｅ	粉末	－	酢酸	0.5	80	10	2
実施例1a	樹脂Ｅ	a	80	－	－	－	10	2
実施例1b	樹脂Ｅ	a	80	酢酸	0.5	20	10	2
実施例1c	樹脂Ｅ	a	80	酢酸	0.5	60	10	2
実施例1d	樹脂Ｅ	a	－	酢酸	0.5	80	10	2
実施例２	樹脂Ａ	粉末	－	酢酸	0.5	40	10	1
実施例2a	樹脂Ａ	粉末	70	－	－	－	10	1
実施例2b	樹脂Ａ	粉末	70	硝酸	0.5	20	10	1
実施例2c	樹脂Ａ	粉末	70	硝酸	0.5	70	10	1
実施例2d	樹脂Ａ	粉末	－	硝酸	0.5	70	10	1

【表２】

樹脂中の不純物濃度(ppm)

	Na元素		K元素		Fe元素		Cr元素		Cu元素	
	処理前、後		処理前、後		処理前、後		処理前、後		処理前、後	
実施例1	20	0.01	30	0.02	10	0.05	50	0.01	10	0.01
実施例1a	20	0.1	30	0.1	10	1	50	2	10	1
実施例1b	20	0.06	30	0.04	10	0.1	50	0.3	10	0.1
実施例1c	20	0.01	30	0.02	10	0.05	50	0.01	10	0.01
実施例1d	20	0.1	30	0.1	10	0.1	50	0.5	10	0.2
実施例2	100	0.05	800	0.03	10	0.1	4	0.02	1	0.01
実施例2a	100	0.1	800	0.2	10	1	4	1	1	0.8
実施例2b	100	0.07	800	0.06	10	0.5	4	0.7	1	0.4
実施例2c	100	0.05	800	0.03	10	0.1	4	0.02	1	0.01
実施例2d	100	0.2	800	0.5	10	0.5	4	0.2	1	0.3

実施例３～１２

上記実施例１および実施例２に準じて、各種の電子部品用樹脂について、表３に示すような条件でそれぞれ洗浄処理し、含有していた不純物の除去・低減化を行った。一方、比較のため、従来の純水（常温）による洗浄処理の場合も、その処理条件を表３に併せて示す。さらに、これらの洗浄処理（不純物除去）に当たって当初の不純物濃度（ppm）および処理後の不純物濃度（ppm）を表４にそれぞれ示した。

【００２８】なお、表１において、試料の状態ａは酢酸エチル20%溶液の場合を、また

樹脂Ａ：tert- ブトキシカルボニル化ビニルフェノール樹脂

樹脂Ｂ：ポリビニルフェノール樹脂

樹脂Ｃ：tert- ブトキシカルボニルメトキシ化ビニルフェノール樹脂

樹脂Ｄ：ポリイソプロペニル化フェノール樹脂

樹脂Ｅ：m-クレゾールノボラック樹脂

の場合をそれぞれ示す。

【００２９】

【表３】

	樹脂	試料の状態	酸水溶液中の酸	酸濃度 (M)	処理条件 温度 (℃)	時間 (分)	回数
実施例3	樹脂A	a	酢酸	2	60	20	1
実施例4	樹脂B	a	酢酸	0.5	70	10	2
実施例5	樹脂C	粉末	硝酸	0.1	60	20	1
実施例6	樹脂D	粉末	硝酸－塩酸－フッ化水素	0.1	60	10	1
実施例7	樹脂D	a	酢酸	1	70	10	2
実施例8	樹脂D	a	乳酸	1	70	10	2
実施例9	樹脂E	粉末	硝酸－塩酸	2	25	10	1
実施例10	樹脂E	粉末	硝酸－塩酸－フッ化水素	0.5	50	10	2
実施例11	樹脂E	a	乳酸	1	80	10	2
実施例12	樹脂E	粉末	硝酸－塩酸－フッ化水素	1	40	20	1
比較例1	樹脂A	粉末	純水	－	20	10	2
比較例2	樹脂A	a	純水	－	20	10	2
比較例3	樹脂D	粉末	純水	－	20	10	2
比較例4	樹脂D	a	純水	－	20	10	2
比較例5	樹脂E	粉末	純水	－	20	10	2
比較例6	樹脂E	a	純水	－	20	10	2

【表4】

樹脂中の不純物濃度(ppm)

	Na元素		K元素		Fe元素		Cr元素		Cu元素	
	処理前	後	処理前	後	処理前	後	処理前	後	処理前	後
実施例3	100	0.03	300	0.02	10	0.05	5	0.1	5	0.1
実施例4	70	0.4	100	0.1	5	0.1	8	0.08	1	0.1
実施例5	50	0.1	20	0.1	2	0.2	1	0.8	1	0.1
実施例6	20	0.1	40	0.1	2	0.1	10	0.1	10	0.07
実施例7	80	0.6	10	0.1	10	0.5	10	0.2	5	0.1
実施例8	200	0.1	200	0.03	15	0.02	7	0.05	5	0.03
実施例9	100	0.08	150	0.04	20	0.1	5	0.1	1	0.1
実施例10	50	0.08	80	0.04	10	0.04	5	0.08	1	0.02
実施例11	20	0.1	50	0.1	5	0.1	1	0.1	1	0.1
実施例12	10	0.1	30	0.1	10	0.06	1	0.05	1	0.08
比較例1	100	10	150	80	20	8	10	2	10	3
比較例2	100	5	200	50	10	3	4	1	5	0.8
比較例3	20	1	60	10	10	1	10	3	1	0.8
比較例4	80	1	100	20	5	0.5	10	3	1	0.3
比較例5	60	0.5	100	10	5	0.2	5	2	3	1
比較例6	80	0.8	50	10	10	4	5	1	0.8	

【００３０】

【発明の効果】以上説明したように本発明に係る不純物の除去方法によれば、レジスト樹脂中の金属系の各不純物元素を 0.1ppm 程度以下と、容易に除去・低減することが可能となる。つまり、煩雑な操作など要せずに、かつ短時間の洗浄処理で従来法に比較して、10倍以上の除去効率で高純度のレジスト樹脂を調製することが可能になる。

【図面の簡単な説明】

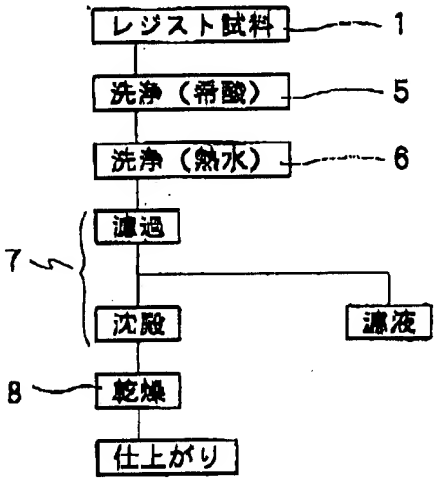
【図１】本発明に係る電子部品用樹脂中の不純物除去方法例を示すフローチャート図。

【図２】従来のレジスト樹脂中の不純物除去方法を示すフローチャート図。

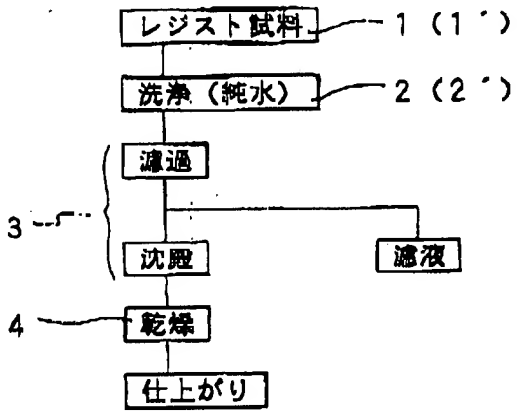
【符号の説明】

１，１′…レジスト試料　２，２′…洗浄（純水…常温）工程　３，７…レジスト試料分離工程　４，８…乾燥処理工程　５…洗浄（希酸水）工程　６…洗浄（熱水）工程

【図１】


レジスト試料
1
洗浄（希酸）
5
洗浄（熱水）
6
濾過
7
沈殿
濾液
8
乾燥
仕上がり

【図２】


レジスト試料
1（1´）
洗浄（純水）
2（2´）
濾過
3
沈殿
濾液
4
乾燥
仕上がり

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(54) [Title of the Invention]

METHOD FOR REMOVING IMPURITY IN RESIN FOR ELECTRONIC PART

(57) [Abstract]

[Object]

It is an object of the present invention to provide a method for removing an impurity in

a resin for an electronic part, which can remove and reduce an impurity in a resin for an electronic part easily so that the concentration of each impurity element of metal system is less than or equal to 0.1 ppm.

[Structure]

The present invention is characterized by having a step of at least performing one of hot water treatment and dilute-acid treatment on a resin for an electronic part containing an impurity to remove the contained impurity; and a step of separating the resin for the electronic part in which the contained impurity is removed with preventing an impurity from intruding, and drying, whereby a super high purity positive resist composition which has, for example, concentration of an impurity element of metal system of several tens of 10 ppb level can be obtained.

[Scope of Claim]

[Claim 1]

A method for removing an impurity in a resin for an electronic part characterized by comprising steps of:

performing at least one of hot water treatment and dilute-acid treatment on a resin for an electronic part containing an impurity to remove the contained impurity; and

separating the resin for the electronic part in which the contained impurity is removed with preventing an impurity from intruding, and drying.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a method for removing an impurity in a resin for an electronic part, and in particular, relates to a method for removing an impurity in a resin for an electronic part which is effective for removing and reducing an impurity of metal system such as iron or sodium contained in a resin.

[0002]

[Related Art]

For example, in manufacture of an integrated circuit, a negative resist using cyclized isoprene rubber as a material or a positive resist using a novolac resin as a material is generally used in pattering an active element or the like. In recent years, as the integration degree of an

integrated circuit is improved, a positive photosensitive resin which is superior in resolution has been used more often.

[0003]

However, when an impurity of metal system such as alkali metal or heavy metal is present (contained) in the photoresist resin, even if the amount of the impurity is small, the impurity become the cause of defective in pressure of an insulating oxide film, a PN junction leakage fault, and the like. That is, a slight amount of an impurity of metal system contained in the photoresist resin used in a manufacturing step of an ULSI has a significant impact on the functional reliability of the finally manufactured USIL. Accordingly, in such a photoresist resin, it is desired that an impurity of metal system be removed as possible.

[0004]

In accordance with the above request, in general, washing operation with pure water (room temperature) by the procedure shown in FIG.2 is performed, whereby the impurity in the photoresist resin is removed and reduced. Specifically, for example, a method in which an photoresist resin is dissolved in an organic solvent such as alcohol or acetone, and this resin solution 1 is dropped in a large amount of stirring pure water (room temperature) to perform stirring washing treatment 2 , only resin component is subject to precipitation-filtration separating treatment 3 and drying treatment 4 is performed, or a method in which a photoresist resin is dissolved in a non-water-soluble solvent such as ethyl acetate or toluene, only an impurity is extracted and removed by intensively stirring washing the resin solution with pure water (room temperature), then the non- water-soluble solvent is removed, and drying treatment 4 is performed, can be given. These washing operation methods usually repeat the washing operation and lower the concentration of impurity to the acceptable range.

[0005]

It is to be noted that, though the influence of an impurity of metal system in a photoresist resin and a method for removing and reducing the impurity are illustrated in the above, for example, also in a case of a sealing resin of a semiconductor device, a resin for a protective film, or a resin for interlayer insulating of multilayer wiring, the problem cannot be ignored in view of performance and function required for a device to which they are applied (used).

[0006]

[Problems to be Solved by the Invention]

The above washing method using pure water with room temperature can promote removing and reducing of an impurity included in a resin; however, it is difficult to remove an alkali metal element or a heavy metal element efficiently yet. For example, it has been difficult to remove and reduce the concentration of each impurity element of metal system to be equal to or less than 0.1ppm. That is, concentration of impurity element of metal system can be reduced relatively easily to some extent by repeating washing operation with room-temperature pure water; however, once after the concentration reaches slight amount of approximately 1ppm, the efficiency in removing and reducing the concentration of an impurity element of metal system is low even though the number of repetition of the washing operation is increased to a large extent; and it is clear that there is a limitation in terms of practical use.

[0007]

The present invention is made to cope with such a condition and it is an object to provide a method for removing an impurity in a resin for an electronic part, which can remove and reduce an impurity in a resin for an electronic part easily so that the concentration of each impurity element of metal system is less than or equal to 0.1ppm.

[0008]

[Means for Solving the Problem]

A method for removing an impurity in a resin for an electric part according to the present invention is characterized by having a step of performing at least one of hot water treatment and dilute-acid treatment on a resin for an electronic part containing an impurity to remove the contained impurity; and a step of separating the resin for the electronic part in which the contained impurity is removed with preventing an impurity from intruding, and drying.

[0009]

In addition, this invention is made on the basis of the view that when either hot water treatment or dilute-acid treatment is performed, an impurity in a resin can be removed and reduced easily so that the concentration of each metal impurity element is less than or equal to 0.1 ppm as a result of keenly examining and studying a method for removing and reducing a slight amount of metal impurity contained in a resin for a electronic part such as a photoresist

resin.

[0010]

In the present invention, as a resin for an electronic part containing an impurity which is to be an object to be treated, any resist resin manufactured by any conventionally known method may be acceptable, and for example, a rubber based resist resin such as polyisoprene or polybutadiene, an acrylic based resist resin such as acrylic acid ester or methacrylic acid ester, a phenolic based resist resin such as novolac, and the like can be given. In addition, it is more effective that a resist resin in which a concentration of the contained resin sensitively affects on sensitivity and pattern profile , for example, a chemically-amplified resist having sensitivity to the environment is an object to be treated.

[0011]

As such a chemically-amplified resist resin, for example, there are a phenolnovolac resin type, a cresolnovolac resin type, a xylenolnovolac resin type, a vinylphenol resin, an isopropenylphenol resin, a copolymer of a vinylphenol and acrylic acid, methacrylic acid derivative, acrylonitrile, styrene derivative, and the like, a copolymer of isopropenylphenol and acrylic acid, methacrylic acid derivative, acrylonitrile, styrene derivative, and the like, and the like; specifically, for example, a poly(p-vinylphenol), a copolymer of p-isopropenylphenol and nitrile (copolymerization ratio: 1:1), a copolymer of p-isopropenylphenol and styrene (copolymerization ratio: 1:1), a copolymer of p-vinylphenol and methylmethacrylate(copolymerization ratio: 1:1), a copolymer of p-vinylphenol and methylstyrene (copolymerization ratio: 1:1), and the like can be given.

[0012]

Further, the resist resin is suitable for treatment in which a hydroxyl group of a polymer is substituted by a photosensitive substituent group such as acetoxy, formyloxy, methacrylanilide, o-nitrobenzyl, dihydropyridyl, o-quinonediazide sulfonic acid, acryloyl, diazonium, sulfonium, iodonium, organic halide, or a protecting group of carboxylic acid containing tertiary carbon such as tert-butyl ester and tert-butyl carbonate, a protecting group containing secondary carbon such as cyclohexyl, a sec-butyl group, an isopropyl group, a protecting group such as a trialkyl group, a phenylsilyl group, a tetrahydropyranyl group, a methylmethoxy group, and the like in order to control developing solution resolvability and to give photosensitivity using an alkali

metal compound as a reaction reagent.

[0013]

As an impurity contained in the resin for an electronic part, for example, iron (Fe), sodium (Na), potassium (K), copper (Cu), and the like can be given. These metal impurities are represented as ions as followings: for example, iron (2+ or 3+), sodium (1+), potassium (1+), and copper (1+ or 2+).

[0014]

It is necessary that purity of the hot water (pure water), acid, solvent, and the like used in the present invention be as highly as possible. It is desirable that each have the following metal impurity concentrations: for example, iron: less than or equal to 5ppb, sodium: less than or equal to 10ppb, potassium: less than or equal to 10ppb, and copper: less than or equal to 5ppb. Further, the temperature condition in a case where hot water (pure water) is used for predetermined washing treatment is more than or equal to approximately 35°C, preferably more than or equal to 40°C, whereby the effect of hot water is obtained since the higher the temperature is set the more washing effect is improved. It is necessary that the higher limit be set so that a resin to be treated is not dissolved by heat. It is generally preferable that the higher limit be set as the temperature which is lower by 20°C than the heat dissolving temperature of the resin to be treated. In addition, though there is no particular limit on the used amount of hot water (pure water), it is desirable that the same or more amount of water as the amount of the resin to be treated be selected to achieve more adequate washing effect.

[0015]

On the other hand, in a case where a dilute acid aqueous solution is used for the predetermined washing treatment, the concentration of the dilute acid aqueous solution is selected and set in view of the stability to the acid of a resin to be treated. For example, in a case of a chemically-amplified resist material having acid cross-linking or an acid decomposing group, it is set to be approximately 0.1 to 0.5 M. Then, this kind of a dilute acid aqueous solution can be prepared by making a solution by adding at least one kind of acid selected among, for example, the high-purity of nitric acid, hydrochloric acid, fluorinated acid, citric acid, tartaric acid, lactic aid, and the like to high-purity water. It is to be noted that the washing treatment using a dilute acid aqueous solution may be performed at room temperature; however, a metal

impurity can be removed and reduced more efficiently by heating washing process system using a dilute acid aqueous solution to be more than or equal to, for example, 40°C.

[0016]

In addition, in either case, chromium, zinc, copper, or the like, for example, can be removed and reduced by the selection of ph control of washing treatment system and an organic solvent (washing treatment in which a resin to be treated is made to be a solution).

[0017]

In the present invention, it goes without saying that a material from which impurity is not eluted such as tefron, synthetic quartz (or structure with coating with these materials), or the like is used or that working environment (atmosphere) is considered so that a washing device (container or instrument), a separating device, a drying device, and the liked used in a series of operation such as the washing treatment is prevented from being new source of contamination.

[0018]

[Operation]

According to the above method of the present invention, a resin for an electronic part containing impurities such as, for example, sodium or potassium contacted with hot water (pure water) or a dilute acid aqueous solution first, whereby performing washing treatment. Then, in a case of washing process using hot water (pure water), activation energy is improved by the heat and the contained element which is easy to be dissolved such as sodium or potassium is quickly ionized, moved into the hot water easily and separated from the resin; therefore, removing and reducing of an impurity in a resin for an electronic part is achieved. In addition, also in a case where washing treatment is performed using a dilute acid aqueous solution, a cathode ion in the dilute acid aqueous solution is quickly reacted with an impurity such as, for example, iron (2+ or 3+) and copper (1+ or 2+); therefore, removing and reducing of an impurity in a resin for an electronic part is achieved. Further, also in the case of the washing treatment using a dilute acid aqueous solution, activation energy is improved by heating and the efficiency of removing and reducing an impurity is enhanced. It is to be noted that washing is performed more uniformly in a case where a resin to be treated is a solution than in a case where a resin to be treated is powdery; accordingly, efficiency of removing an impurity becomes generally higher in the former case.

[0019]

[Embodiment]

Hereinafter, the present invention will be explained more specifically with embodiments; however, the present invention is not be limited to the embodiments, and it goes without saying that modifications can be made properly without departing from the scope of the present invention.

[0020] Embodiment 1

First, 100 g of an m-cresol novolac resin with the following concentrations of impurities was stored in a container made of teflon: Na: 20 ppm, K: 30 ppm, Fe: 10 ppm, Cr: 50 ppm, and Cu: 10 ppm. Further, 500 g of a 0.5 M acetic acid aqueous solution was added thereto and washing treatment was performed by intensive shaking and stirring for 10 minutes, keeping warming (heating) at 60°C. Then, after the resin component was filtrated using a filter made of teflon and the washing treatment was performed again, the resin component was filtrated using the filter made of teflon. It is to be noted that 2 l of pure water was used to fully remove the acetic acid used in the washing treatment at this time.

[0021]

The resin component which was subject to the washing treatment and filtration was stored in a vacuum drying apparatus and drying treatment was performed at 50°C for 2 days, whereby removing of an impurity in the resin was completed. When the concentrations of impurities in the powder of the resin to which impurity removing treatment were performed in the above manner was measured using a flameless atomic absorption device, it was found that the concentrations of impurities were drastically removed and reduced to be as follows: Na: 10 ppb, K: 20 ppb, Fe: 50 ppb, Cr: 10 ppb, and Cu: 10 ppb.

[0022]

It is to be noted that, each result of carrying out the following experiments using a prepared solution in which 100 g of an m-cresol novolac resin was diluted in 400 g of acetic acid ethyl with the conditions shown in the table 1 which is based on the conditions of the above washing treatment is shown in table 2 along with the case of embodiment 1: washing treatment using hot water (embodiment 1a), washing treatment using hot water - acid solution of room temperature (embodiment 1b), washing treatment using hot water - hot acid solution

(embodiment 1c), and washing treatment using a hot acid solution (embodiment 1d).

[0023]

As will be appreciated from the above embodiment, efficiency of removing impurities is higher in a case where the washing treatment system was kept warm (heated) than in a case where the washing treatment system was set at room temperature. In addition, the effect of removing sodium and potassium was high in the case of hot-water washing. Further, as shown in a flowchart of FIG. 1, in the above embodiment, in a case where a hot-water washing treatment step 6 was added after a washing treatment step 5, and a filtration - separating treatment step 7 and a drying treatment step 8 were performed, the removing and reducing of impurities was performed further efficiently.

[0024] Embodiment 2

First, a solution prepared by dissolving 100 g of a tert-butoxycarbonylated vinylphenol resin having concentrations of impurities of: Na: 100 ppm, K: 300 ppm, Fe: 10 ppm, Cr: 4.0 ppm, and Cu: 1.0 ppm in 400 g of acetic acid ethyl was stored in a container made of teflon. Further, 500 g of a 0.5 M acetic acid aqueous solution was added thereto and washing treatment was performed by intensive shaking and stirring for 10 minutes keeping warming (heating) at 40°C. Then, the solution was left at rest to separate a resin solution and an acid aqueous solution into two layers and the resin solution of an upper layer was removed. After a solvent (acetic acid ethyl) was distilled away from this resin solution, 400 g of acetone was used to make a solution again. Then, the solution was dropped in 3 l of pure water and precipitated again. Thereafter, the resin component was filtrated using a filter made of teflon. Then, the filtrated resin component was stored in a vacuum drying apparatus and drying treatment was performed at 50°C for 2 days, whereby removing of impurity in the resin was completed. When the concentrations of impurities in the powder of the resin to which impurity removing treatment was performed in the above manner were measured using a flameless atomic absorption device, it was found that the concentrations of impurities were drastically removed and reduced to be as follows: Na: 50 ppb, K: 300 ppb, Fe: 100 ppb, Cr: 20 ppb, and Cu: 10 ppb.

[0025]

It is to be noted that, each result of carrying out the following experiments using powder of a tert-butoxycarbonylated vinylphenol resin without making the resin into a solution with the

conditions shown in the table 1 which is based on the conditions of the above washing treatment is shown in table 2 along with the case of embodiment 2: washing treatment using hot water (embodiment 2a), washing treatment using hot water - acid solution of room temperature (embodiment 2b), washing treatment using hot water - hot acid solution (embodiment 2c), and washing treatment using a hot acid solution (embodiment 2d).

[0026]

As will be appreciated from the above embodiment, efficiency of removing impurities is higher in a case where the washing treatment system was kept warm (heated) than in a case where the washing treatment system was set at room temperature. In addition, the effect of removing sodium and potassium was high in the case of hot-water washing.

[0027]

[Table 1]

	kind of resin	condition of sample	temperature of hot water (°C)	acid in a dilute acid aqueous solution	concentration of acid (M)	temperature of acid (°C)	Treatment conditions	
							time (min)	number
Embodiment 1	resin E	powder	-	acetic acid	0.5	60	10	2
Embodiment 1a	resin E	a	60	-	-	-	10	2
Embodiment 1b	resin E	a	60	acetic acid	0.5	20	10	2
Embodiment 1c	resin E	a	60	acetic acid	0.5	60	10	2
Embodiment 1d	resin E	a	-	acetic acid	0.5	60	10	2
Embodiment 2	resin A	powder	-	acetic acid	0.5	40	10	1
Embodiment 2a	resin A	powder	70	-	-	-	10	1
Embodiment 2b	resin A	powder	70	nitric acid	0.5	20	10	1
Embodiment 2c	resin A	powder	70	nitric acid	0.5	70	10	1
Embodiment 2d	resin A	powder	-	nitric acid	0.5	70	10	1

[Table 2]

Concentrations of impurities in resins (ppm)

	Na element		K element		Fe element		Cr element		Cu element	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Embodiment 1	20	0.01	30	0.02	10	0.05	50	0.01	10	0.01
Embodiment 1a	20	0.1	30	0.1	10	1	50	2	10	1
Embodiment 1b	20	0.06	30	0.04	10	0.1	50	0.3	10	0.1
Embodiment 1c	20	0.01	30	0.02	10	0.05	50	0.01	10	0.01
Embodiment 1d	20	0.1	30	0.1	10	0.1	50	0.5	10	0.2
Embodiment 2	100	0.05	300	0.03	10	0.1	4	0.02	1	0.01
Embodiment 2a	100	0.1	300	0.2	10	1	4	1	1	0.8
Embodiment 2b	100	0.07	300	0.06	10	0.5	4	0.7	1	0.4
Embodiment 2c	100	0.05	300	0.03	10	0.1	4	0.02	1	0.01
Embodiment 2d	100	0.2	300	0.5	10	0.5	4	0.2	1	0.3

Embodiments 3 to 12

Washing treatment was performed with the conditions shown in table 3 to various kinds of resins for electronic parts based on the above embodiment 1 and embodiment 2, whereby contained impurities were removed and reduced. On the other hand, treatment conditions in a case of washing treatment with conventional pure water (room temperature) is also shown in

table 3 for comparison. Further, the concentrations (ppm) of impurities before and the concentrations (ppm) after these washing treatments (impurity removal) are shown in table 4.

[0028]

It is to be noted that, in table 1, condition a of a sample shows each of a case of a solution with 20 % of acetic acid ethyl and a case where: resin A: tert-butoxycarbonylated vinyl phenol resin, resin B: polyvinyl phenol resin, resin C: tert-butoxycarbonylmethoxylated vinyl phenol resin, resin D: polyisopropenylated phenol resin, and resin E: m-cresolnovolac resin.

[0029]

[Table 3]

	kind of resin	condition of sample	acid in a dilute acid aqueous solution	concentration of acid (M)	treatment conditions		
					temperature (°C)	time (min)	number
Embodiment 3	resin A	a	acetic acid	2	50	20	1
Embodiment 4	resin B	a	acetic acid	0.5	70	10	2
Embodiment 5	resin C	powder	nitric acid	0.1	50	20	1
Embodiment 6	resin D	powder	nitric acid - hydrochloric acid - hydrogen fluoride	0.1	50	10	1
Embodiment 7	resin D	a	acetic acid	1	70	10	2
Embodiment 8	resin D	a	lactic acid	1	70	10	2
Embodiment 9	resin E	powder	nitric acid - hydrochloric acid	2	25	10	1
Embodiment 10	resin E	powder	nitric acid - hydrochloric acid - hydrogen fluoride	0.5	50	10	2
Embodiment 11	resin E	a	lactic acid	1	80	10	2
Embodiment 12	resin E	powder	nitric acid - hydrochloric acid - hydrogen fluoride	1	40	20	1

Comparative example 1	resin A	powder	pure water	-	20	10	2
Comparative example 2	resin A	a	pure water	-	20	10	2
Comparative example 3	resin D	powder	pure water	-	20	10	2
Comparative example 4	resin D	a	pure water	-	20	10	2
Comparative example 5	resin E	powder	pure water	-	20	10	2
Comparative example 6	resin E	a	pure water	-	20	10	2

[Table 4]

Concentrations of impurities in resins (ppm)

	Na element		K element		Fe element		Cr element		Cu element	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Embodiment 3	100	0.03	300	0.02	10	0.05	5	0.1	5	0.1
Embodiment 4	70	0.4	100	0.1	5	0.1	3	0.06	1	0.1
Embodiment 5	50	0.1	20	0.1	2	0.2	1	0.3	1	0.1
Embodiment 6	20	0.1	40	0.1	2	0.1	10	0.1	10	0.07
Embodiment 7	30	0.5	10	0.1	10	0.5	10	0.2	5	0.1
Embodiment 8	200	0.1	200	0.03	15	0.02	7	0.05	5	0.03

Embodiment 9	100	0.06	150	0.04	20	0.1	5	0.1	1	0.1
Embodiment 10	50	0.06	30	0.04	10	0.04	5	0.06	1	0.02
Embodiment 11	20	0.1	50	0.1	5	0.1	1	0.1	1	0.1
Embodiment 12	10	0.1	30	0.1	10	0.06	1	0.05	1	0.06
Comparative example 1	100	10	150	30	20	3	10	2	10	3
Comparative example 2	100	5	200	50	10	3	4	1	5	0.8
Comparative example 3	20	1	50	10	10	1	10	3	1	0.3
Comparative example 4	80	1	100	20	5	0.5	10	3	1	0.3
Comparative example 5	60	0.5	100	10	5	0.2	5	2	3	1
Comparative example 6	30	0.3	50	10	10	4	5	1	0.3	

[0030]

[Effect of the Invention]

As explained above, according to the method of removing an impurity of the present invention, it is possible to easily remove and reduce each impurity element of metal system in a resist resin to be less than or equal to approximately 0.1ppm. That is, it is possible that a resist resin with high purity can be prepared with removing efficiency, which is greater than or equal to ten times than a conventional method, with washing treatment for a short time without complicated operations.

[Brief description of the Drawings]

[FIG. 1] A flowchart showing an example of a method for removing an impurity in a resin for an electronic part according to the present invention.

[FIG. 2] A flowchart showing a conventional method for removing an impurity in a resist resin.

[Explanation of Reference]

1 and 1': resist sample, 2 and 2': washing (pure water at room temperature) step, 3 and 7: resist sample separating step, 4 and 8: drying treatment step, 5: washing (dilute acid water) step; and washing (hot water) step.